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<b>(21) International Application Number:</b> PCT/US91/04993 <b>(22) International Filing Date:</b> 19 July 1991 (19.07.91) <b>(30) Priority data:</b> 563,223                      6 August 1990 (06.08.90)                      US <b>(71) Applicant:</b> PFIZER INC. [US/US]; 235 East 42nd Street, New York, NY 10017 (US). <b>(72) Inventors:</b> BAUER, Roger, E. ; 3415 Kathleen Avenue, Allentown, PA 18103 (US). MATHUR, Krishna, K. ; 505 Farm View Drive, Easton, PA 18042 (US). <b>(74) Agents:</b> RICHARDSON, Peter, C. et al.; Pfizer Inc., Patent Department, 235 East 42nd Street, New York, NY 10017 (US).		<b>(81) Designated States:</b> AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> CALCIUM CARBONATE TREATED WITH FATTY ACIDS, MANUFACTURE AND USE		
<b>(57) Abstract</b>  Precipitated calcium carbonate, having an average particle size of from about 0.01 micron to about 0.1 micron, and a specific surface area of from about 10 m <sup>2</sup> /g to about 100 m <sup>2</sup> /g, surface treated with at least one high molecular weight unsaturated fatty acid, such as erucic acid, or a combination of at least one high molecular weight unsaturated fatty acid, and at least one high molecular weight saturated fatty acid, wherein the preferred combination of a high molecular weight unsaturated fatty acid and a high molecular weight saturated fatty acid is oleic acid and erucic acid, respectively, and processes for the preparation of such material are disclosed. A method for the addition of such surface-treated calcium carbonate to polyvinyl chloride plastisols to increase the baked adhesion of the plastisol to a metal surface and to reduce the baking temperature at which the plastisol formulation is baked onto the metal surface is also disclosed.		

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<sup>+</sup> It is not yet known for which States of the former Soviet Union any designation of the Soviet Union has effect.

## 5     Calcium carbonate treated with fatty acids, manufacture and use

Background of the Invention

This invention broadly relates to treated filler  
10 materials, more particularly, to surface-treated calcium  
carbonate, and still more particularly to calcium carbonate  
surface-treated with a high molecular weight unsaturated  
fatty acid for use as filler in polyvinyl chloride  
plastisols to improve the baked adhesion to electrocoated  
15 metal surfaces at low bake temperatures.

Polyvinyl chloride (PVC) plastisols are generally  
composed of finely divided PVC resin, plasticizers and  
fillers; for particular application they may contain small  
amounts other additives such as stabilizer, pigments or  
20 colorants, and adhesion promoting compounds. The components  
of a plastisol are combined and mixed to form a fluid which  
may be applied to a substrate (e.g. cloth or metal) or  
formed into shapes or articles (e.g. gloves). After this,  
the plastisol is heated, which results in the complete  
25 diffusion of plasticizer into the resin particles (gelation)  
over the temperature range of from about 50°C to about  
170°C, and in the melting of the polymer over the  
temperature range of from about 120°C to about 180°C. When  
the melted (fused) plastisol is then allowed to cool below  
30 about 50°C, it forms a flexible, tough and chemical-  
resistant solid.

In the automotive industry, PVC plastisols may be used  
as undercoatings, chip guards and as sealants for the seams  
of welded metal parts. The body work and underside of autos  
35 are generally electrocoated primed sheet metal; plastisols  
for these applications must adhere well to the electrocoated  
metal and must have good abrasion and impact resistance to  
perform their protective and sealant functions. Since PVC  
homopolymer has relatively poor inherent adhesion to  
40 electrocoated metal, vinyl acetate copolymers which have  
fast gelation times and low fusion temperatures are

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substituted for a portion of the homopolymer resin. Because copolymers undergo quicker viscosity aging (increase in viscosity) and develop lower ultimate impact strength properties than homopolymers, the amount of homopolymer they  
5 can replace is limited. Therefore organic adhesion promoting compounds are often added to automotive type plastisols.

Recently there has been a trend in the automotive industry to bake PVC plastisols at lower temperatures (i.e.  
10 about 120°C) than was formerly the practice (i.e. 140-150°C). This energy-cost saving step, in which the paint coating is often baked simultaneously with the plastisol, has put the processing temperature near to the minimum needed for fusion. Since complete fusion is necessary for  
15 the development of optimum physical properties, including adhesion, the use of lower bake temperatures has made plastisol formulation more critical.

Calcium carbonate is used in PVC plastisols in the forms of ground limestone and precipitated calcium carbonate  
20 (PCC). Ground limestone is added as a filler, primarily to reduce the volume cost of the plastisol. Precipitated calcium carbonate is used to increase the low shear viscosity and thixotropy of the fluid plastisol and to increase the impact resistance of the baked product.  
25 Surface treatment of the calcium carbonate with stearic acid or salts of stearic acid is widely practiced for decreasing the plasticizer absorption and increasing the compatibility of the calcium carbonate.

PCC, treated with stearic acid or salts of stearic  
30 acid, manufactured by Pfizer Inc., New York, and commercially available under the name Ultra-Pfplex, was tested in a polyvinyl chloride plastisol of the type used in the automotive industry for performance with respect to rheology and adhesion. The plastisols made with Ultra-Pfplex  
35 had unacceptably poor baked adhesion to electrocoated metal when the bake temperature was around 120°C.

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It was then decided to experiment with different combinations of PCC treated with other materials to determine whether there would be improvement in baked adhesion at low baking temperature by using such other  
5 treated PCC's as a functional filler material in PVC plastisols.

Further work involving pre-surface-treating the PCC with high molecular weight unsaturated fatty acid or a combination of a high molecular weight unsaturated fatty  
10 acid and a high molecular weight saturated fatty acid, has resulted in the discovery of the present invention.

#### Summary of the Invention

It has been discovered that unexpectedly, the addition to a polyvinyl chloride plastisol of a precipitated calcium  
15 carbonate which has been pre-surface treated with a high molecular weight unsaturated fatty acid or a combination of a high molecular weight unsaturated fatty acid and a high molecular weight saturated fatty acid, greatly increases the baked adhesion of the overall composition to an  
20 electrocoated metal surface, especially when the baking process is conducted at a low baking temperature in the range of from about 115°C to about 125°C.

#### Detailed Description of the Invention

The PCC for surface treatment according to preferred  
25 embodiments of the present invention has an average particle size of from about 0.01 to about 0.1 micron, and preferably about 0.07 micron. The PCC has a specific surface area in the range of from about 10 m<sup>2</sup>/g to about 100 m<sup>2</sup>/g, depending on the corresponding average particle size. For PCC with an  
30 average particle size of 0.07 micron, the specific surface area is from about 18 m<sup>2</sup>/g to about 22 m<sup>2</sup>/g.

The PCC filler material is surface treated according to the present invention with at least one high molecular weight (C<sub>≥</sub>20) unsaturated fatty acid or a combination of at  
35 least one high molecular weight (C<sub>≥</sub>18) unsaturated fatty acid and at least one high molecular weight (C<sub>≥</sub>20) saturated fatty acid.

It has been discovered that when the PCC is surface-treated with a high molecular weight unsaturated fatty acid alone, the fatty acid must have a carbon content of at least C=20 in order to provide both the desired adhesion and rheological properties. However, when the PCC is surface-treated with a combination of at least one high molecular weight unsaturated fatty acid at at least one high molecular weight saturated fatty acid, it is possible to utilize an unsaturated fatty acid having a somewhat lower carbon content of at least C-18 to provide adhesion, as long as the high molecular weight saturated fatty acid has a carbon content of at least C=20, to provide the rheological properties. While use of unsaturated fatty acids having a carbon content lower than C=18 still affords a fair amount of adhesion in the PVC plastisol to which the calcium carbonate coated with such acid has been added, it has been found that the rheological properties of a PVC plastisol incorporating a calcium carbonate coated with a less than C<sub>18</sub> unsaturated fatty acid become less and less acceptable with decreasing carbon content. The high molecular weight unsaturated fatty acid, when utilized alone, is selected from the group consisting of erucic acid (cis-13-docosenoic acid), gadoleic acid (9 cis-eicosenoic acid), brassidic acid (13 trans-docosenoic acid), selacholeic acid (15 cis-tetrasenoic acid), ximenic acid (17 cis-hexacosenoic acid), lumegueic acid (21 cis-triacon-tenoic acid), and combinations thereof. Where a high molecular weight unsaturated fatty acid is used in combination with the unsaturated fatty acid, it is possible to utilize an unsaturated fatty acid selected from the above indicated group and further including oleic acid (C<sub>18</sub>). It has been found, according to the present invention, that erucic acid (cis-13-docosenoic acid) is preferred as the unsaturated fatty acid when used alone. The high molecular weight saturated fatty acid is selected from the group consisting of arachidic acid (C<sub>20</sub>), behenic acid (C<sub>22</sub>), lignoceric acid (C<sub>24</sub>), cerotic acid (C<sub>26</sub>), montanic acid (C<sub>28</sub>), and

combinations thereof. A preferred combination of a high molecular weight unsaturated fatty acid and a high molecular weight saturated fatty acid is oleic acid and behenic acid.

The PCC is surface-treated with the unsaturated fatty acid or acids or combination of unsaturated and saturated fatty acids to the extent of from about 1.0 weight percent to about 3.5 weight percent based on the weight of the calcium carbonate. Preferably, the fatty acid surface treatment is present in an amount of about 2.0 weight percent to about 2.5 weight percent, based on the weight of calcium carbonate.

Surface treatment of the PCC with the unsaturated or combination of unsaturated and saturated fatty acids according to the present invention is accomplished by either a dry process or a wet process.

In the dry process, ultrafine precipitated calcium carbonate at room temperature is first dry-mixed alone until the frictional heating produced by mixing causes an increase in the temperature of the PCC to about 80°C. At that point, a sufficient amount of at least one high molecular weight unsaturated fatty acid or a combination of at least one high molecular weight unsaturated fatty acid and at least one high molecular weight saturated fatty acid, is added to the PCC to produce a coating of the fatty acid on the PCC of from about 1.0 to about 3.5 weight percent based on the weight of PCC. Mixing of the PCC and the fatty acid is continued until the temperature rises to about 105°C due to frictional heating, or at least five minutes have elapsed since addition of the fatty acid. The coated ultrafine PCC is then ready for milling to any desired degree of fineness, using, for example, a Mikroatomizer mill (Mikropul Division, Hosokawa Micron International, Inc., Summit, N.J.).

In the wet process, ultrafine precipitated calcium carbonate is first mixed with water to form a slurry. Preferably, the PCC is as a centrifuge paste containing about 40.1% by weight of calcium carbonate. The PCC-water

slurry is heated to 85°C and agitated for about one hour to produce a homogeneous mixture. A sodium salt solution of at least one high molecular weight unsaturated fatty acid or a combination of sodium salt solutions of at least one high molecular weight unsaturated fatty acid and at least one high molecular weight saturated fatty acid is then added to the slurry, with agitation, over a period of about 5 minutes. The resulting new slurry is agitated for about one hour at a temperature around 85°C and is then dewatered, such as by filtration, dried at a temperature around 110°C and milled, such as with a Mikroatomizer mill.

Preferably, the high molecular weight fatty acid is erucic acid. A sodium erurate solution is prepared by saponifying erucic acid with an excess of sodium hydroxide. Erucic acid is a solid at room temperature. In the dry mixing process, the PCC and the erucic acid are combined and homogenized in a high intensity mixer, such as a Henschel type mixer (Rheinstahl Henschel AG, Kassel, W. Germany) or a Welex type mixer (Gunther Pappenmeier GmbH, Detmold, W. Germany).

The components are mixed sufficiently long to allow complete melting of the erucic acid and its uniform adsorption by the calcium carbonate. The calcium carbonate is then deagglomerated in a high speed mill such as a Mikroatomizer mill.

Addition of an effective amount of an erucic acid surface-treated PCC filler to a PVC plastisol, namely, an amount of from about 10 weight percent to about 30 weight percent, based on the weight of the plastisol, and preferably, from about 15 weight percent to about 20 weight percent, based on the weight of the plastisol, has been found to greatly increase the baked adhesion of the filled plastisol to an electrocoated metal, particularly when the baking step is performed at a low temperature in the range of from about 110°C to about 140°C, and preferably at about 120°C.



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While not wishing to be limited to a particular theory, it is believed that addition of a precipitated calcium carbonate treated with a high molecular weight saturated fatty acid or a combination of a high molecular weight unsaturated fatty acid and a high molecular weight saturated fatty acid to a polyvinyl chloride plastisol improves the rheological properties and adhesion of the plastisol to an electrocoated metal surface because the high molecular weight of the coating agent on the PCC has a beneficial effect on the product rheology, and because the unsaturation of the coating agent on the PCC improves the bake adhesion of the plastisol to the metal surface and enables the plastisol to set at a lower baking temperature than heretofore utilizable with the plastisol alone.

An amine type adhesion promoter may also be added to the surface-treated PCC-PVC plastisol mixture to further improve the baked adhesion of the mixture to a metal surface. When an amine type adhesion promoter is used, it is added to the surface-treated PCC-PVC plastisol mixture in an amount of from about 0.8 weight percent to about 1.0 weight percent, based on the weight of the PCC-PVC plastisol mixture. The amine type adhesion promoter is selected from the group consisting of amino-amides, such as Euretek 550, 556, 580 and 600, manufactured by Sherex Corp., Dublin, OH, and amino functional silanes, as manufactured by Union Carbide Corp., Danbury, CT.

The nature of the present invention may be more fully understood in light of the following non-limiting examples.

#### Example 1

#### Preparation of Ultrafine PCC Surface-treated with Various Levels of Erucic Acid by Dry-Method

Samples of ultrafine PCC were surface treated with erucic acid in amounts of 1.5%, 2.0%, 2.25%, and 2.5% by weight, based on the weight of PCC.

The samples were prepared by surface-treating ultrafine PCC which had previously been synthesized, dewatered and

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dried. The source of the PCC was from the Pfizer Inc. plant at Adams, MA.

The dried samples of Ultrafine PCC were surface-treated with the erucic acid at the various levels in a laboratory 5 scale Welex high intensity mixer. The Ultrafine PCC was first placed into the Welex mixer and mixed alone at a blade speed of 3800 rpm until the temperature reached 80°C.

At that point, erucic acid (Prifrac 2990, Unichema Chemicals Inc., Chicago, IL) was added and mixing was 10 continued at 3800 rpm until the temperature of the batch reached 105°C or five minutes had elapsed from the time of the erucic acid addition. The amounts of each ingredient for the various samples are shown in Table I.

Table I

15	<u>Sample No.</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
	Erucic Acid Wt. %	1.50	2.00	2.25	2.50
	Ultra fine PCC (gms)	1970	1960	1955	1950
	Erucic acid (gms)	30.0	40.0	45.0	50.0

After surface treatment, the samples were 20 deagglomerated in a Mikroatomizer Mill (Mikropul Div., Hosokawa Micron International, Inc., Summit, NJ).

Example 2

Evaluation of Samples of Erucic Acid surface-treated PCC in PVC Plastisol

25 The samples of Ultra fine PCC surface-treated with various levels of erucic acid, prepared in Example 1, were added to a polyvinyl chloride plastisol of the type used in the automotive industry to evaluate the properties of the material as to adhesion and rheology.

30 Each of the surface treated PCC samples of Example 1 was evaluated in the PVC plastisol formulation shown in Table II.

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Table II

PVC Plastisol Formulation Containing Erucic Acid Treated Ultrafine PCC.

	<u>Component</u>	<u>Amount (gms)</u>	<u>Weight Percent</u>
5	PVC Resin Oxychem 6338 (Occidental Chemical Co., Pottstown, PA)	220	31.94
10	Plasticizer, Santicizer 711 (Monsanto Co., St. Louis, MO)	220	31.94
15	Adhesion Promoter, Euretek 580 Sherex Chemical Co., Dublin, OH)	5.36	0.78
20	Calcium Oxide, Technical grade (Fisher Scientific Co., Fairlawn, NJ)	9.90	1.44
	Limestone, Vicron 25-11 (Pfizer Inc., NY, NY)	110	15.97
25	Mineral Spirits, Industrial grade	13.5	1.96
30	Erucic acid surface-treated PCC(Samples 1-4, from Table I)	110	15.97
	Total	<u>688.76</u>	<u>100.00</u>

The plastisol formulations were mixed using a Ross  
 35 double planetary mixer (Charles Ross and Son Co., Hauppauge,  
 NY). The resin plasticizer, calcium oxide and adhesion  
 promoter were placed in the mixing bowl and mixed at 55 rpm  
 for three minutes. The limestone and erucic acid treated  
 ultrafine PCC were added and mixing continued at 55 rpm for  
 40 twenty minutes. The mineral spirits were then added and  
 mixing continued at 55 rpm for five minutes under vacuum.  
 Water was circulated through the jacket of the mixing bowl  
 throughout the mixing procedure. Each of the final plastisol  
 formulations was packed in a can and stored 24 hours at  
 45 72°F.

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After this conditioning period, the viscosity of each batch was measured using a Brookfield Model HBT Viscometer using the TE spindle and the Model D Helipath stand (Brookfield Engineering Laboratories, Stoughton, MA). The results are shown in Table III.

Table III

<u>Sample No.</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Viscosity @ 5 rpm (cps)	512,000	472,000	408,000	400,000
Viscosity @ 50 rpm (cps)	81,600	76,000	69,000	66,000
10 Yield =	43,000	40,000	34,000	33,000
<u>2 (5rpm) (V<sub>5</sub>-V<sub>50</sub>)</u> 100				

Immediately after the viscosity measurements were completed, the adhesion properties of each plastisol were measured. A  $0.050 \pm 0.002$  inch thick film, of each sample of plastisol was applied to an ED 3060 (PPG Automotive Products Inc., Cleveland, OH) electrocoated metal test panel. The film was applied to a 2-inch wide by 3 inch long rectangular area of the panel. The panels were then placed in an oven at 120°C for 30 minutes. After removal from the oven, the panels were allowed to stand at room temperature for 30 minutes. At that time, two parallel slits were made in the plastisol film 0.5 inch apart and through the entire width of the film. A spatula was used to lift a small piece of the strip thus formed and an attempt was made to slowly pull the test strip from the metal test panel. If the strip could be entirely removed leaving no residue on the panel, the adhesion was rated poor. If the strip tore before detaching from the panel, the adhesion was rated excellent (i.e. greater than the cohesion of the plastisol). The results of this test for the various samples is shown in Table IV.

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Table IV

<u>Sample No.</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Adhesion	Excellent	Excellent	Excellent	Excellent
Relative Adhesion				

5 (Interpretation of results)

Table IV shows that although all of the erucic acid surface treated PCC containing PVC plastisol formulations according to the present invention demonstrated superior baked adhesion to an electrocoated metal surface, the  
10 adhesion increased with increasing amount of erucic acid on the PCC.

Example 3Wet Coating Calcium Carbonate with Erucic Acid

Three gallons of tap water and 5,095 grams of ultrafine  
15 precipitated calcium carbonate centrifuge paste containing 40.1% by weight of calcium carbonate were combined in a stainless steel container to form a first slurry. The components were heated to 85°C with agitation and further agitated for about 1 hour at 85°C after which a sodium  
20 erucate solution was added with agitation over a period of about 5 minutes, forming a second slurry.

The sodium erucate solution was prepared by saponifying erucic acid with an excess of sodium hydroxide. 53.12 grams of erucic acid (Prifrac 2990, Unichema Chemicals Inc.,  
25 Chicago, Ill.) were added with agitation to 3090 ml of tap water which had been heated to 85°C. 12.58 grams of 50% (weight/weight) sodium hydroxide aqueous solution, representing a 5% excess of NaOH was added. The resultant solution was agitated for one hour at 85°C before addition  
30 to the PCC slurry.

The second slurry was agitated for one hour at 85°C after which it was dewatered by filtration, dried at 110 °C and milled with a Mikroatomizer mill.

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CLAIMS

1. A composition characterized by calcium carbonate surface-treated with at least one high molecular weight unsaturated fatty acid or at least one high molecular weight saturated fatty acid.

2. The composition according to claim 1 further characterized by the calcium carbonate having an average particle size of from about 0.01 to about 0.1 micron.

3. The composition according to claim 1 further characterized by the calcium carbonate having a specific surface area of from about 10 m<sup>2</sup>/g to about 100 m<sup>2</sup>/g.

4. The composition according to claim 1 further characterized by the condition that when at least one high molecular weight unsaturated fatty acid is utilized alone, it is selected from the group consisting of erucic acid (cis-13-docosenoic acid), gadoleic acid (9 cis-eicosenoic acid), brassidic acid (13 trans-docosenoic acid), selacholeic acid (15 cis-tetrasenoic acid), ximenic acid (17 cis-hexacosenoic acid), lumegueic acid (21 cis-tri-acontenoic acid), and combinations thereof; and when at least one high molecular weight unsaturated fatty acid is utilized in combination with at least one high molecular weight saturated fatty acid, the unsaturated fatty acid is selected from the group consisting of oleic acid, erucic acid (cis-13-docosenoic acid), gadoleic acid (9 cis-eicosenoic acid), brassidic acid (13 trans-docosenoic acid), selacholeic acid (15 cis-tetrasenoic acid), ximenic acid (17 cis-hexacosenoic acid), lumegueic acid (21 cis-tri-acontenoic acid), and combinations thereof.

5. The composition according to claim 4 further characterized by the high molecular weight unsaturated fatty acid being erucic acid.

6. The composition according to claim 1 further characterized by the high molecular weight saturated fatty acid being selected from the group consisting of arachidic

acid (C<sub>20</sub>), behenic acid (C<sub>22</sub>), lignoceric acid (C<sub>24</sub>), cerotic acid (C<sub>26</sub>), montanic acid (C<sub>28</sub>), and combinations thereof.

7. The composition according to claim 1 further characterized by the high molecular weight unsaturated fatty acid being oleic acid and the high molecular weight saturated fatty acid being behenic acid.

8. The composition according to claim 1 further characterized by the high molecular weight unsaturated fatty acid or combination of high molecular weight saturated fatty acid and high molecular weight saturated fatty acid being from about 1.0 weight percent to about 3.5 weight percent, based on the weight of calcium carbonate.

9. The composition according to claim 8 further characterized by the high molecular weight unsaturated fatty acid or combination of high molecular weight unsaturated fatty acid and high molecular weight saturated fatty acid being from about 2.0 weight percent to about 2.5 weight percent, based on the weight of calcium carbonate.

10. A process for preparing calcium carbonate surface-treated with at least one high molecular weight unsaturated fatty acid or a combination of at least one high molecular weight unsaturated fatty acid and at least one high molecular weight saturated fatty acid, characterized by the steps of:

a) dry-mixing an ultrafine precipitated calcium carbonate to raise the temperature thereof due to frictional heating to about 80°C;

b) adding to the calcium carbonate a sufficient amount of at least one high molecular weight unsaturated fatty acid or a combination of at least one high molecular weight unsaturated fatty acid and at least one high molecular weight saturated fatty acid, to ultimately produce a desired level of fatty acid coating on the calcium carbonate;

c) mixing the calcium carbonate and fatty acid until the temperature thereof increases to about 105°C due to frictional heating and continuing said mixing for at least

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5 minutes from the time of addition of the fatty acid to the calcium carbonate; and

d) milling the fatty acid-coated calcium carbonate.

11. A process for preparing calcium carbonate surface-treated with at least one high molecular weight unsaturated fatty acid or a combination of at least one high molecular weight unsaturated fatty acid and at least one high molecular weight saturated fatty acid, characterized by the steps of:

10 a) mixing an ultrafine precipitated calcium carbonate with water to form a first slurry;

b) heating the first slurry to a temperature of about 85°C while agitating the slurry;

c) adding to the first slurry, with continuous agitation, a sufficient amount of a saponified sodium salt solution of at least one high molecular weight unsaturated fatty acid or combination of at least one high molecular weight unsaturated fatty acid and at least one high molecular weight saturated fatty acid, to ultimately produced a desired level of fatty acid coating on a calcium carbonate, to form a second slurry;

d) maintaining the temperature of the second slurry at about 85°C and further agitation for about one hour to homogenize the second slurry;

25 e) dewatering the second slurry;

f) drying the dewatered second slurry at a temperature of about 110°C; and

g) milling the dried second slurry.

12. A method for improving the rheological properties of polyvinyl chloride plastisols and increasing their baked adhesion to coated metal surfaces, particularly at low bake temperature, characterized by forming a mixture by adding to said plastisol and homogeneously mixing therewith, an effective amount of calcium carbonate has been surface-treated with a high molecular weight unsaturated fatty acid or a high molecular weight unsaturated fatty acid in combination with a fatty acid ester, applying said mixture



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to a coated metal surface, and baking at a temperature in the range of from about 115°C to about 150°C.

13. The method according to claim 12 further characterized by the amount of surface-treated calcium carbonate being from about 10 weight percent to about 30 weight percent, based on the weight of the plastisol.

14. The method according to claim 13 further characterized by the amount of surface-treated calcium carbonate being from about 15 weight percent to about 20 weight percent, based on the weight of the plastisol.

15. The composition according to claim 1 further characterized by from about 0.8 percent by weight to about 1.0 percent by weight of an amine-containing adhesion promoter.

16. The composition according to claim 15 further characterized by the amine-containing adhesion promoter being selected from the group consisting of amino-amides and amino-functional silanes.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/04993

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C09C1/02; C09C3/08; C08K9/04		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C09C ; C08K	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>9</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	EP,A,0 377 149 (DEUTSCHE SOLVAY-WERKE) 11 July 1990 see page 2, line 32 - page 3, line 21 see page 4, line 2 - line 10 ---	1-3,8-10
X	DE,C,958 830 (S.A. DU BLANC OMYA) 28 February 1957 see page 2, paragraph 4; claims 1,2 ---	1,10
X	CHEMICAL ABSTRACTS, vol. 100, no. 4, 23 January 1984, Columbus, Ohio, US; abstract no. 24008T, page 70 ; column R ; & JP-A-58120519 (HAMADA M.) 18.07.1983 see abstract --- -/--	1
<p><sup>9</sup> Special categories of cited documents : <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
16 DECEMBER 1991	06 JAN 1992	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	VAN BELLINGEN I. <i>John Bellingen</i>	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
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# ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

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The members are as contained in the European Patent Office EDP file on  
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		JP-A- 2228349	11-09-90
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82